Extended summaries 9th International Congress of Pesticide Chemistry

The following are Extended Summaries based on material from poster presentations at the 9th International Congress of Pesticide Chemistry, organised by the International Union of Pure and Applied Chemistry (IUPAC) and held in London, UK, 2–7 August 1998. They are entirely the responsibility of the authors and do not necessarily reflect the views of the Editorial Board of Pesticide Science.

β-Methoxyacrylates; synthesis of new types of strobilurin fungicides with extended side chains

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Abstract: A series of novel oxime ether β-methoxyacrylates have shown good fungicidal activity against a number of fungal pathogens. These were designed by introducing a one- or two-atom spacer group adjacent to the oxime ether group. Best fungicidal activity was obtained when an amino spacer group was used.

Keywords: strobilurins; β-methoxyacrylates; azoxystrobin; mitochondrial respiration

The strobilurin family of natural products are derivatives of β-methoxyacrylic acid and are found in several genera of small fungi such as *Strobilurus tenacellus*. The fungicidal activity of the strobilurins (including strobilurin A (**1**, Fig 1)) arises from their ability to inhibit mitochondrial respiration by blocking electron transfer between cytochromes b and c_1.[1]

Work in Zeneca led to the discovery of azoxystrobin (**2**)[2] which is sold as a broad-spectrum systemic fungicide. Strobilurins of type **3** gave rise to a new generation of active fungicides in which the oxime ether bond provided a mimic for the pyrimidine ring of **2**.[3] Further series of active strobilurins were prepared in which a 'spacer' group was inserted between the aromatic ring and the oxime ether bond (**4**).

It was envisaged that strobilurins of type **8** (Fig 2) could be prepared from reaction of oximes of type **5** with the benzyl bromide (**6**). Unfortunately, this led to the formation of undesired products (**7**), due to the oxime anion (**9**) fragmenting to give the nitroso diene (**11**, Fig 3) and the phenoxide or thiophenoxide (**10**) which then reacted with the bromide (**6**).

This problem was overcome by reaction of *N*-hydroxyphthalimide (**12**, Fig 4) with the benzyl bromide (**6**) to give the strobilurin (**13**)[4] which, upon treatment with hydrazine and the requisite methyl ketone gave the desired analogues of **8**.[5]

Reversal of the spacer atoms produced another active series of strobilurins (**16**, Fig 5). These were prepared from the reaction of acetaldoxime (**14**, Fig

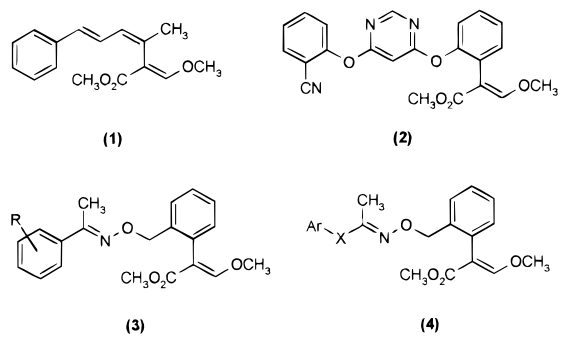

Figure 1. Strobilurin A (**1**), Azoxystrobin (**2**), arylheterocyclic (**3**) and extended oxime ethers (**4**).

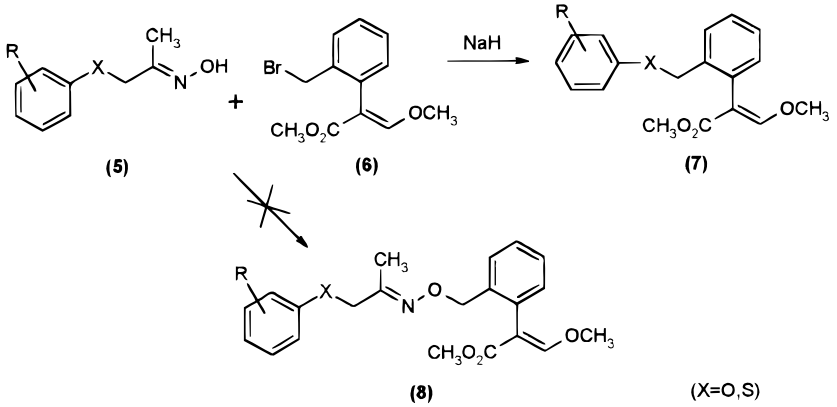

Figure 2. Problems of oxime fragmentation.

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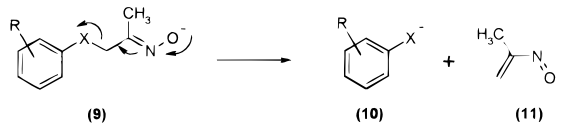

Figure 3. Mechanism of oxime fragmentation.

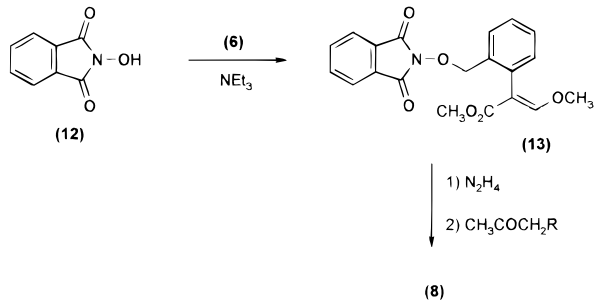

Figure 4. Preparation of extended strobilurins of type **8**.

5) with *N*-chlorosuccinimide followed by sodium methane thiolate to give the oxime **15**. Reaction of **15** with **6** in the presence of sodium hydride, followed by oxidation of the sulfur and displacement of methylsulfonate with the alkoxy/thioalkoxy anion afforded the desired products, **16**.[6]

A further class of active strobilurins prepared were the 'oxyamidines' (**19**, Fig 6). These were synthesized by the reaction of a variety of anilines (**17**, Fig 6) or heterocyclic equivalents with trimethylorthoformate and zinc chloride to give the imidates **18**. Reaction of the oxyphthalimide **13** with hydrazine followed by **18** produced the desired products, **19**.[7]

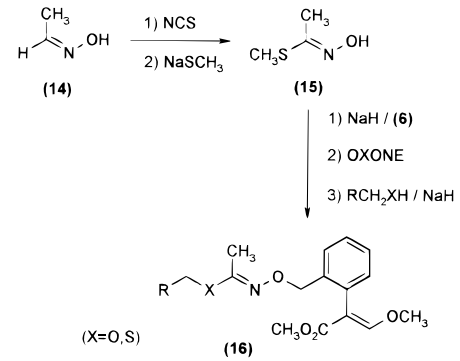

Figure 5. Preparation of extended strobilurins (**16**).

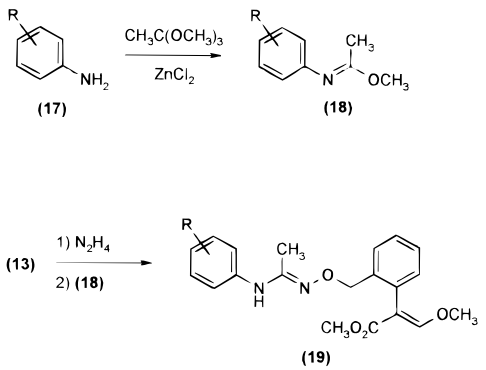

Figure 6. Preparation of oxyamidines **19**.

Good levels of activity amongst all three series of strobilurins was found against a broad spectrum of fungal pathogens in glasshouse tests, examples being *Erysiphe graminis* DC, *Plasmopara viticola* Berl & de Toni and *Septoria nodorum* Berk. The 'oxyamidine' series (**19**) also showed excellent activity against *Puccinia recondita* Rob.ex Desm. and *Venturia inequalis* (Cooke) Wint.

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The effects of six adjuvants on the rainfastness of chlorpyrifos formulated as an emulsifiable concentrate

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Abstract: The chemically different adjuvants 'Agral', 'Bond', 'Codacide Oil', Li 700, 'Silwet L'-77, and 'Headland Guard' were assayed to determine their effects on the rainfastness of an emulsifiable concentrate formulation of the organophosphorus pesticide chlorpyrifos. Cabbage leaves were each treated with 200 × 0.25-μl droplets of diluted formulation using a hand-held microapplicator. Droplet deposits were left to air-dry for 1 h prior to exposure to simulated rainfall. Rain fastness was assessed using GC residue analyses of treated leaves after exposure to 10, 20 or 30 min simulated rainfall. The results indicated that the latex-based adjuvants 'Bond' and 'Headland Guard' induced a statistically significant increase in rainfastness, results for the other adjuvants assayed being either not significant or inconclusive. The results are discussed within the context of using adjuvants to enhance insecticide efficacy.

Keywords: rainfastness; chlorpyrifos; adjuvants; organophosphate

1 INTRODUCTION

To maximise their biological efficacy many pesticides have to be able to withstand, following applica-

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